


VERIFICATION OF TRANSLATION

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I, the undersigned,

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hereby declare that I am the translator of the specification and claims of International Patent Application PCT/IB2004/003795 and certify that I am competent with both the French and English language and that the following is a true translation to the best of my knowledge and belief.



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May 4, 2006

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PLASMA THIN-FILM DEPOSITION METHOD

10 MAY 2006

The present invention concerns a method for plasma depositing a thin-film on a surface to be treated. In particular, the invention relates to the depositing of organic or polymeric films, especially to achieve imperviousness of the surface to be treated.

Plasma methods for depositing a thin film on the surface of an object to be treated are already known and used in various areas, e.g. for depositing thin layers on semiconductors such as described in American patent US 5,569,502, for depositing impervious layers or barriers on the surface of PET bottles such as described in international application PCT/IB02/01001, for depositing films on fabrics such as described in European patent EP 1 024 222, for depositing edible impervious films on foodstuffs such as described in WO 96/22030.

In many of these applications, it is sought to deposit very thin layers with a view to the advantages they provide, such as flexibility, transparency, the possible forming of multilayers, their non-impact on the general characteristics of the object to be treated, or for other properties.

For ingestible products, such as foodstuffs or pharmaceutical products, a very thin layer offers the advantage of being undetectable by the consumer.

In the area of textiles, very thin layers have the advantage of being highly flexible and able to maintain their integrity despite the major deformations undergone by objects made in fabrics, such as clothing. It is important however that this layer should be uniform to guarantee its imperviousness or other desired properties over the entire surface to be treated.

Plasma thin-film deposition methods often concern the depositing of inorganic films resulting from plasmachemical reactions of particles (ions, atoms, radicals, activated particles) derived from a precursor gas or mixture of precursor gases activated by a plasma. Most proposed methods are conducted in a partial vacuum to gain better control over plasma parameters and development conditions of the thin layer. Vacuum methods are extremely costly however for industrial applications and mass production. In addition, the presence of a vacuum has the disadvantage of affecting the properties of the object to be treated (e.g. dehydrating the objects to be treated). A further problem encountered when forming thin layers with known plasma methods is the creation of undesired powder on the treated surface.

Although inorganic films are desired in numerous applications, it will also be of advantage to be able to form thin films in organic or polymeric materials especially, but not only, in the area of ingestible products such as edible or pharmaceutical products. While some inorganic materials are permitted in small quantities in foods, and proposed by application WO 9622030 for example, there is a general desire to avoid their use as much as possible. The presence of elements in the human body such as debris of inorganic films containing different metals in oxide form may have harmful consequences. In addition, the method described in the above-cited application uses a vacuum plasma, a method that is costly and hardly suitable for mass production. Experience has also shown that the method of depositing inorganic films on the surfaces to be treated of foods, fabrics, paper or other items whose geometry and surface properties may vary quite extensively, is extremely difficult to control in reliable manner.

Regarding the area of foodstuffs, protective layers against oxidation (oxygen barrier) or against moisture loss or absorption (water and water vapour barrier) are highly sought after and various methods for depositing organic films, such as layers of cellulose, polydextrose, lipids or proteins have been put forward in the prior art. Known methods for depositing organic films on edible products do not use plasma however and give rise to layers whose thickness is insufficiently thin to go undetected or whose barrier properties are not very good or reliable.

Patent application WO 87/03453 for example proposes the use of organic deposits, such as cellulose and lipid layers to protect edible products. These layers are deposited in the form of a solution or liquid suspension and are then dried. Aside from the difficulty in depositing a very thin film forming a good barrier using this method, the drying process is costly and may have harmful effects on the object to be treated.

US 6,312,740 proposes depositing a layer in the form of an electrostatically charged edible powder on the surface of foodstuffs, a corona discharge being used to charge the powder particles. It is mentioned that the ideal particle size is in the order of 120 μm , such sizes still being perceived however by the consumer.

It is to be pointed out that the efficacy of the deposited layers is determined by their thickness, their density and their adhesion to the surface to be treated. When depositing a film on edible products, the increase in the thickness of the layer leads to a change in the taste of the protected product.

Experience has shown that particles having a size of over 1 μm can be perceived. This means that the protective layer must be ultra-thin, if possible less than 0.5 μm . For

foodstuffs, it is also sought to achieve layers which do not contain any toxic product, which do not affect the taste of the product and which, for most applications, are not water soluble.

5 No method proposed to date satisfactorily meets these requirements.

 These thin layer properties are also sought for applications in other areas, e.g. for proofing fabrics or paper, depositing a film on bottles and packaging, in
10 particular for foods or pharmaceuticals, or for other applications.

 In the light of the above, one purpose of the invention is to provide a method for depositing a film on a surface to be treated, the film being very thin, uniform and effective,
15 the method being adapted for industrial production, in particular for the treatment of objects that are mass produced.

 It is of advantage that the method and device for implementing the method should not be costly.

20 It is of advantage to provide a method and device for implementing the method with which it is possible in reliable manner to deposit thin layers on objects of different shapes and sizes or having complex surfaces..

 It is of advantage to provide a method for depositing a
25 thin film that contains no or scarcely any inorganic components, in particular in the food and pharmaceutical sectors.

 It is of advantage to provide a method for depositing a film on various foods or pharmaceutical products or other
30 products that are ingested, which can be implemented on a production line at reasonable cost.

 It is of advantage, for some applications, to provide a method for depositing a very thin layer, less than 1 μm in

particular, in organic or polymeric matter on the surface to be treated of various materials.

Another purpose of the invention is to provide an impervious film for foods, pharmaceutical products or other
5 ingestible products that is effective, reliable and harmless.

A further purpose of the invention is to provide organic or polymeric coatings that are very thin, uniform and effective, in particular coatings forming a barrier against liquids or gases.

10 Some purposes of the invention are attained using the method as in claim 1.

In the present invention, the film depositing process is based on the generation of a plasma in a mixture of inert plasmagenic gas and precursor gases and then spraying the
15 resulting gas (plasma) onto the surface to be treated. The precursor gases contain at least two components.

A first component comprises saturated organic substances or a mixture of saturated organic substances.

A second component contains unsaturated organic
20 substances or a mixture of unsaturated organic substances.

The composition of precursor gases includes carbon and/or hydrogen and/or halogenic elements.

The unsaturated organic substances are the main source of heavy, free, multivalent radicals. These chiefly form the
25 building blocks of the polymeric chain.

The saturated organic substances, subsequent to plasmochemical processes in the plasma zone, come to be the main source of light, free radicals with a single free bond. These radicals are responsible for halting the development of
30 the polymeric chain.

The heavy multivalent radicals are more adsorbed on the surface. This means that the ratios between the quantities of building blocks and single-bond radicals are different on the

surface to be treated and within the volume. Firstly this gives rise to a shortened polymeric chain and hence to limited formation of powder within the volume, and secondly to intensified film depositing on the surface.

5 Film depositing is stimulated by prior activation of the surface.

Another major advantage of this method is that it can be conducted under atmospheric pressure and does not therefore require any pump or vacuum enclosure, thereby simplifying the
10 equipment needed for implementing the method in an industrial environment, in particular for treating mass produced objects. The use of two precursor gases or mixtures of precursor gases according to the invention, also makes it possible to achieve a high film depositing rate, higher than depositing rates when
15 using vacuum plasma methods.

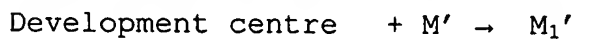
The inventive method also has the advantage of positioning the electric discharge to create the plasma, at a relatively long distance away from the surface to be treated, which optimises the yield of the method and avoids the problem
20 of overheating the object to be treated. The radicals derived from the at least two precursor gases or mixtures of precursor gases enter the plasma and live for a certain time, corresponding to the maximum migration time to bring the radicals to the surface to be treated for plasmochemical
25 reaction therewith. This optimal distance is also determined by the need to activate the surface to be treated with ionised particles and ultraviolet radiation, and with the activated atoms formed by the plasma.

To obtain protective polymeric films on product surfaces,
30 food products for example, it is advantageous to use as precursors the gases consisting of C_kH_l , C_mF_n or $C_sH_pF_r$ or their mixtures. The formation of the protective film is determined by volume and surface plasmochemical processes.

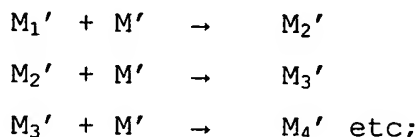
The surface processes take place on the surface of the object to be treated, in several steps:

- Formation of development centres on the surface to be treated, previously activated by the plasma. This surface may be smooth or rough, or even highly uneven since the activated medium acting on the surface under atmospheric pressure, especially out of thermodynamic equilibrium, may have very low viscosity determining penetration of the active components between the surface irregularities.

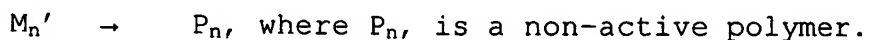
- Genesis (initiation) of chains due to the depositing of active multivalent free radicals, derived from the heavy precursor gas or gas mixture, on the surface to be treated:



- Chain development:



- Rupture of the chain by monovalent radicals derived from the light precursor gas or gas mixture :



In this way it can be seen that the formation of the polymeric layer on the surface of the product to be treated comprises the formation of "building blocks" in the plasma zone, the migration of these blocks towards the surface, and the formation of a polymeric layer not containing free radicals on the surface.

Evidently the formation of polymeric powders within the volume and the formation of the polymeric layer on the surface compete with one another. This competition is solved in particular through the choice of components for the mixture of precursor organic gases.

For example, advantageously a mixture of an unsaturated component is used such as hexafluoropropylene (C_3F_6) and a saturated component such as tetrafluoromethane (CF_4).

The CF_4 , when entering the plasma, in particular forms
5 light radicals CF_3' . It is these radicals which halt the formation of the polymeric chains.

The C_3F_6 forms the heavy biradicals $(CF_3-CF-CF_2)''$ which are the polymer building blocks.

In principle, these reactions take place within the
10 volume and on the treated surface. The competition between the volume and surface formation of polymers is determined by the ratio between the concentrations of heavy and light radicals. On the surface the concentration of heavy biradicals prevails over that of light radicals, which promotes the formation of
15 the polymeric film on the treated surface.

In the volume, the concentration of CF_3' light radicals prevails over that of heavy radicals. This slows down the formation of polymeric powders therein.

By varying the proportions of these components
20 empirically, the experiments conducted under the invention show that it is possible to practically exclude the formation of powder in the volume.

The use of fluoro-organic precursors, such as in the above-cited example, allows the formation of a film of
25 polytetrafluoroethylene $(-CF_2-CF_2-)_n$ on the surface to be treated.

The polytetrafluoroethylene film (also commonly known as "Teflon") is a film having very good moisture and oxygen barrier properties, and is a harmless material and hence well
30 suitable for uses in the area of edible products, whether for depositing a film on food products or on wrapping for the packaging of food products or drinks.

Other halogen-organic precursors may also be used for the formation of polymeric layers on a surface to be treated. However since the presence of chlorine in ingestible products is generally not desirable, polymeric layers containing chlorine are to be used in non-food areas.

Under the invention, it is also possible to use hydrocarbons as precursor gas with which to form polymeric films on the surface to be treated, in particular branched polyethylene $(-\text{CH}_2-\text{CH}_2-)_n$.

If the precursor product is a mixture containing carbon, fluorine (or another halogen) and hydrogen, a copolymerisation reaction is obtained.

One important advantage of the inventive method is the possibility of properly controlling the formation of polymeric layers on the surface of the object to be treated, avoiding volume growth, hence obtaining layers of highly uniform thickness. The high uniformity of the deposited layers implies that very thin layers, even monomolecular i.e. in the order of 0.5 nanometres, are well distributed on the surface to be treated. Since the development of the layer on the surface to be treated takes place on the surface and not within the volume, layers of greater thickness can also be deposited with extensive uniformity, the thickness of the layers possibly being controlled for example by varying the treatment time.

Under the invention, it is also possible to form a multilayer film, i.e. formed of layers of different compositions by injecting different precursor gases in sequence during plasma treatment. The mechanism allowing the development of polymeric layers on the surface also has the advantage of eliminating free radicals, which permits the use of the method for edible products. To conclude, the polymeric films formed by the method of the invention are chemically stable, biocompatible, impervious to gases and water, have high elasticity and

mechanical solidity and have good dielectric qualities. Their thickness can vary depending upon the constraints of the application between 0.5 nm (monomolecular layer) and 0.5 μm , a thickness above which the deposited film may disintegrate and
5 separate from the treated surface.

The generated plasma, depending upon application, is continuous or pulsed. It is supplied by a direct, alternating or high frequency current source, or microwave. The generated plasma is especially effective under pulsed operation.

10 The method may advantageously be implemented using a plasma under atmospheric pressure allowing relatively easy integration of the treatment device in an industrial production line and to perform film depositing at industrial production rates.

15 With the inventive method, a plasma is preferably generated that is not in thermodynamic equilibrium, this plasma lending itself to the efficient formation of layers, even very fine layers, on the surface to be treated at atmospheric pressure. Advantageously it is possible to control
20 the discharge pulses in order to generate shock waves which generate ultrasonic vibrations improving the plasmochemical reactions and destroying the hydrodynamic boundary layer on the surface to be treated. All these elements contribute towards accelerating the film depositing process and
25 increasing its efficacy.

The precursor gases, carrying the elements forming the film, are introduced into the film depositing zone either simultaneously in particular in the form of a mixture, or consecutively in the form of portions of different gas
30 mixtures.

In the former case, the optimal composition of the quantities of the different precursor gases can be achieved empirically.

In the latter case, it is possible, whilst maintaining the opportunity of depositing films of optimal composition containing no or only little powder, to form multilayer films which not only ensure the imperviousness of the film but also
5 its flexibility, solidity and other properties (mechanical, optical, chemical). In this case, the composition of the resulting film varies over its thickness. In particular the film may be considered to be multilayer.

The parameters of the film depositing process, in
10 particular the plasma generation parameters and activation of the surface to be treated, may be adapted so as to kill the microorganisms present on the treated surface at the time of treatment. This property of the present invention is particularly useful when treating food products. During such
15 treatment, these products are not only coated with a protective film preventing the migration of gases (oxygen in particular), vapours (water vapours in particular) and water in liquid phase, but also the migration of microorganisms such as mould or yeast brought by the ambient atmosphere or outside
20 contact.

Devices for implementing the method and examples of treatment are described below with reference to the drawings in which:

Fig.1 is a simplified schematic illustrating a plasma
25 device with two nozzles for local treatment by two-dimensional scanning of the surface to be treated;

Fig.2 is a simplified schematic illustrating a plasma device of the invention, intended to be inserted in an industrial production line;

30 Fig.3 is a simplified schematic, illustrating another variant of a plasma device to be inserted in an industrial production line;

Fig.4 is a simplified schematic, illustrating another variant of a plasma device to be inserted in an industrial production line;

Fig.5 is a simplified schematic, illustrating another variant of a plasma device to be inserted in an industrial production line;

Figs.6 to 11 are photographs of untreated and treated food products, illustrating the water imperviousness of the products treated with the plasma methods of the invention, compared with untreated products;

Fig.6 shows drops of coloured water on biscuits;

Fig.7 shows biscuits in water, Fig.7a being a photo taken immediately after immersion, and Fig.7b being a photo taken 20 sec after immersion;

Fig.8 shows biscuits in water, the photo being taken 30 min after immersion;

Fig.9 shows crackers in water, Fig.9a being a photo taken immediately after immersion, and Fig.9b being a photo taken 20 sec after immersion;

Fig.10 shows flaky butter snacks in water, Fig.10a being a photo taken immediately after immersion, and Fig.10b being a photo taken 40 min after immersion; and

Fig.11 shows corn flakes in water, Fig.11a being a photo taken immediately after immersion, and Fig.11b being a photo taken 1 h after immersion.

With reference to Figures 1 to 5, a device for plasma surface treatment to implement a method of the invention comprises one or more plasma generators 15, producing a plasma 4 applied to the surface to be treated 8 that is mobile relative to the plasma generator, either by means of a kinematical system 9 such as a conveyor 10 (Figures 2, 3 and 5) or moving under gravity through a reactor 14 (Fig.4)

subjected to vibrations for example to ensure the controlled flow of the objects to be treated through the reactor.

Referring particularly to Figures 1 and 2, the plasma generator 15 comprises a current source 1, e.g. an alternate
 5 50 Hz current source with a nominal voltage of 1000 V, connected to electrodes 2a, 2b in the form of tubes for example supplied at one end by a plasma formation gas Q_3 and at the other end having nozzles 3a, 3b to direct and influence the form of the generated plasma 4. The plasma generator 15
 10 also comprises a supply system 6 supplying precursor gases Q_1 , Q_2 , this system comprising inlet ducts 6a, 6b, a mixer 6c and an outlet duct 6d. The precursor gas supply system may also be a separate device from the plasma generator, but it is advantageous to integrate this device in the generator or
 15 block of generators so as to better control the passing of precursor gases into the plasma and the resulting components on the surface to be treated 8a.

The outlet duct 6d for the precursor gases and the nozzles 3a, 3b for the plasma formation gas are used to direct
 20 and control the geometric shape of the flow of plasma 4 on the carrier 9 conveying the objects to be treated.

The carrier 9 and/or generator 12 may be mounted on a kinematical system performing a relative movement in one or more directions, so that the flow of plasma 4 scans the
 25 objects to be treated. The kinematical system may be a conveyor in an industrial production line, such as shown Fig. 2 and Figs. 3 and 5 in which the objects to be treated 8 pass through the plasma 4 sprayed towards the conveyor surface.

In the device shown Fig. 2, in order to form a linear
 30 curtain of plasma 4 essentially having the width of the conveyor on which the objects to be treated are positioned, several plasma generators may be mounted side by side in a block of generators 12. The block of generators has ducts to

feed the plasma formation and precursor gases, a current source and a microprocessor controller 13 coupled to the current source in order to control the electric energy supply parameters of the plasma generators.

5 With reference to Fig. 3, it is also possible to arrange plasma generators in the form of plasmotrons along the conveyor either side of the belt 23 of the conveyor, the plasma being enclosed in an enclosure of a reactor delimited by walls 21 and comprising ventilation ducts 22 for residual
10 gases. In this case, the belt 23 of the conveyor may be in the form of a grid or metal mesh to allow treatment by the plasma generated either side of the belt 23 over the entire periphery of the object to be treated. For the surface treatment of
15 Fig. 5, the plasma generators 15 may be arranged underneath the objects to be treated, the hydrodynamic forces of the plasma jets being used to lift and stir the objects to be treated thereby ensuring plasma surface treatment over the entire surface of the object.

20 The stirring and turning of the objects carried on a conveyor may also be achieved by causing the conveyor belt to vibrate and, in this case, it is possible only to provide plasma generators on the upper side of the belt.

 Instead of using a kinematical system to move the objects
25 to be treated, it is also possible to cause them to move through the plasma flows in the enclosure of a reactor 14 under gravity or hydrodynamic force (blown air for example). The reactor 14 may be provided with guiding elements, e.g. in the form of walls 24 to direct the objects to be treated
30 successively into the plasma flows sprayed by the plasma generators 15. The enclosure of reactor 14 is preferably vibrated to ensure the flow of objects to be treated through the orifices 25 formed by the guiding elements which also

control the flow of objects to be treated through enclosure 14. Evacuation of the products to be treated can be directed towards a packaging system 17 mounted on a kinematical system.

5 The plasma generators are preferably placed in the enclosure of a reactor consisting of a casing to insulate the plasma hydrodynamically from the outside environment, so as to better control the plasma flows on the objects to be treated.

10 The plasma generator may be a direct current, alternate current, high frequency or microwave generator. Preferably, the generator is designed to supply the discharge with electric pulses. In this case, it preferably comprises a chopper device in a microprocessor 13 with which to form pulses in amplitude and duration as per the constraints of the method.

15 Examples of the surface treatment of objects, in particular edible products, using methods of the invention are described below.

Example 1

20 The food product to be treated is a sweet biscuit, commonly known under the name "Petit Beurre". The product was placed in the reactor of a device corresponding to Fig. 1. Treatment was conducted under atmospheric pressure.

The parameters were as follows:

- 25 1. Plasmagenic gas: argon
2. Precursor gas: tetrafluoromethane (50%) and
hexafluoropropylene (50%)
3. The discharge supply is made via a high voltage alternate current source. The plasmotron is a plasma
30 generator consisting of two electrodes in the form of nozzles through which the gases arrive in the plasma zone.
4. Start-up voltage of discharge: 10 kV

5. Voltage during discharge: 1÷25 kV
6. Current: 100mA
7. The plasmagenic gas and precursor gases are sprayed into the discharge zone by the electrode nozzles.
- 5 8. The total gas flow rate is ≤ 5 l/min
9. The distance between the electrodes and the treated surface is ~ 4 cm.
10. The linear speed of the treated surface with respect to the plasma is ~ 1 m/min
- 10 11. The scanning speed is 10 cm/min
12. The treatment time is: 30 sec

Results

The composition of the deposited film, which is verified
 15 by infrared spectroscopy, is tetrafluoroethylene (teflon), the mean thickness of the layer being 30 nm.

Using the paramagnetic electronic spectroscopy method, it was found that there is no trace of residual free radicals on the treated surface.

20 The treated biscuits were tested for imperviousness to water. The drops of water deposited on the surface of the untreated biscuit are immediately absorbed. The drops of water deposited on the surface of the treated biscuit are not absorbed. They roll over the surface without being absorbed
 25 such as shown Fig. 6.

The treated and untreated biscuits were immersed in water. The untreated biscuit immediately absorbed water such as shown Fig. 7. The treated biscuit only started to absorb water slowly after 30 min, such as shown Fig. 8.

30 The increase in weight of the biscuits immersed in water for 5 sec was:

- Untreated: 88% ;
- Treated: 0.7 %

Example 2

The product to be treated was "Flaky butter snacks" such
5 as shown Fig. 10.

They were treated using a device such as shown Fig. 1.

The parameters used were those of example 1.

Precursor gas: methane 60%, acetylene 40 %.

10 Results

The thickness of the film obtained was 100 nm. The film
obtained consisted of polyethylene. The tests for water
imperviousness showed that the untreated product absorbs water
in 1 minute. The treated product only absorbed water 40 min
15 after its immersion, such as shown Fig. 10.

The increase in weight of the untreated and treated
products immersed in water for 30 sec, was:

- Untreated: 91 % ;
- Treated: 0.8 %

20

Example 3

The treated product was "Corn Flakes" such as shown Fig.
11. The device used for plasma treatment was of the type
corresponding to Fig. 4.

25 The treatment parameters were:

1. Plasma formation gas: argon
2. Precursor gases : tetrafluoromethane 70 % +
tetrafluorethylene 30 %
3. The plasma generator was a generator with high
30 frequency current ($f = 13.56$ MHz)
4. Power of the plasma generator: 20 kW
5. Treatment time: 30 sec

Results

The treated "Corn Flakes" were coated with a film of Teflon 30 to 40 nm thick. After 5 min the untreated "Corn Flakes" immersed in water lost their shape and properties such as shown Fig. 11a.

The treated "Corn Flakes" had not lost their shape and properties 1 hour after immersion in water, as shown Fig. 11b.

Example 4

10 The treated product was a cereal product of mean diameter 5 mm. Treatment was conducted using a device of the type shown Fig. 5 with "boiling layer".

The plasma formation gas (Ar) was sent onto the conveyor screen mixed with a precursor gas (mixture of methane 60 % and 15 hexafluoropropylene 40 %) creating a "boiling layer" making it possible to properly mix the reactive gas with the product.

Treatment lasted 45 sec.

The treated and untreated products were subjected to water absorption tests. The untreated products lost their 20 properties 5 min after their immersion. The treated products did not lose theirs for one hour after immersion in water.

Example 5

The treated product was a medicinal product, Cimetrol 500 25 LPCI (Metronidazole) in the form of 500 mg tablets. These tablets are highly sensitive to humidity.

Treatment was conducted using a device of the type shown Fig. 5 with a "boiling layer".

Conditions were identical to those for example 4.

30 Treatment lasted 20 sec.

The treated tablets were subjected to water absorption tests. The untreated tablets absorbed water in 2 min. The treated tablets remained intact 10 hours after immersion.

With the treatment it is possible to increase the shelf life of this medicinal product packed in blisters from two months to over two years.

5 Example 6

The treated product was sulfite paper (resin glue 0.5 %; alumina 0.5 %; cooling filler 25 %).

The sample (150 × 150 mm) was placed in the reactor of a device corresponding to Fig. 1.

10 The parameters used were those of example 1.

Plasmagenic gas: argon

Precursor gases: mixture methane (50%) and
hexafluoropropylene (50%).

15 Results

The resistance of the paper was estimated using the stability of its mechanical characteristics during thermal ageing ($T = 100 \pm 3^\circ\text{C}$) for 30 days and exposure of both sides to ultraviolet rays under a UV lamp for 60 min.

20 Tests showed that the solidity and deformation characteristics of the samples remained practically unchanged.

Impregnation through capillarity dropped from 36 mm/10 min for the untreated samples, to 0 for the treated samples. The wettability contact angle of the treated samples was 125
25 degrees.

Example 7

The treated product was a fabric (density - 540 g/m²). The sample (150 × 150 mm) was placed in the reactor of a
30 device corresponding to Fig. 1.

The parameters used were those of example 1.

Plasmagenic gas: argon

Precursor gases: mixture of tetrafluoromethane (75 %)
and hexafluoropropylene (25 %).

Results

5 The oil repelling measurement on the treated sample was
120.

 The drops of water deposited on the surface dried without
impregnating the fabric.

10 Resistance to a column of water after treatment increased
from 0 to 190 cm.

 In other words, the treated sample was highly hydro and
oleophobic.

15 The hydrophobic and oleophobic properties were not
deteriorated after boiling the samples for 1 hour in standard
soapy water.